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PERSPECTIVES OF NANODIAMOND FORMATION FROM THE ORGANIC MATTER AT LOW P-T PARAMETERS

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The perspectives of nanosized diamond particles formation at metastable P-T parameters from organic matter at hydrothermal conditions is discussed. From the known data it's possible to conclude that we could provide the hydrothermal syntheses of nanodiamonds from the water-oil or water-alcohol-oil solutions,

Nowdays for the commercial nanodiamond production detonation methods are used¹. There are few other methods of the formation of nanodiamond particles at laboratory scale. Nanodiamond has been synthesized particularly by chlorination of carbide², electron irradiation of carbon onions³ and in the vapour phase in the substrate-free tube flow CVD reactor⁴.

Meanwhile, Badziag et al.⁵ came to the conclusion that nanometer-sized diamonds could be more stable than graphite when formed from organic compounds - aromatic polycyclic hydrocarbons at low P-T parameters. These hydrocarbons were founded in the meteorite, interstellar diamonds⁶, in the kimberlitic diamonds and carbonados and in oil⁷⁻⁸. Now nanodiamonds are known in the meteorites and interstellar matter (ref.6). Moreover, astronomical observations suggest that as much as 10 to 20% of interstellar carbon is in the form of ultrananocrystalline diamonds⁹. Nakano et al. (ref.6) related interstellar diamond formation with organic matter, which mainly consists of glycolic, eicosanoic and lauric acids, heavy aromatic polycyclic hydrocarbons (phenanthrene) and aromatic hydrocarbons (indene); and nitrogen-bearing organic – acetamides and lactamides. Sellgren¹⁰ identified the relationship between the interstellar diamond and water ice. Based on these relationships Kouchi et al.¹¹ identified new formation routes of diamond in interstellar clouds and parent bodies of carbonaceous chondrites in laboratory experiments. It's the ice mixture of H₂O, CO, NH₃, and CH₄ (4:2:2:1). The questions of when and how does nanodiamonds originate in the cosmos still remain open (ref.1), although comparative microstructural analysis of nanodiamonds extracted from meteorites indicated, that

the majority of cosmic nanodiamonds are formed by low-pressure vapor condensation¹². Also there are foundation of microdiamonds in the organic matrix of the earth crustal rocks^{13,14} and diamond molecules in the crude oil¹⁵. Based on these data Giardini et al. (ref.7) and Zubkov¹⁶ came to the conclusion that the genesis of kimberlitic diamonds and oil are connected with each other in the upper mantle. From the above data it follows that the oil could be the potential source for the nanodiamond formation.

Simakov^{17,18} has shown that nanosized diamond particles could be formed from hydrocarbon fluids at their oxidation and water formation at low temperatures and pressures without seeds. The question of whether diamond could be grown under hydrothermal conditions mimicking those under which it is formed in the Earth has been also long debated^{19,20}. Roy et al.²¹ have made the detailed study of the hydrothermal growth of diamond in the C-H-O and C-H-O-halogen systems. It's also known that water at P-T parameters corresponded to the supercritical water conditions is favourable environment for the diamond growth²². Suitable reactants in gaseous, liquid or solid phase, which contain the elements carbon, hydrogen and oxygen, are added to the supercritical water to form a reactant mixture. The reactants react by oxidation or pyrolysis at the supercritical conditions to produce reactive intermediates, which are necessary for the conversion of the carbon to diamond. They are CH₃, CH₂, CH₃OH, CH₂OH, HO₂, H₂O₂, H, OH²³. The addition (reaction) of alcohols in supercritical water, or the oxidation of hydrocarbons in supercritical water, is likely to produce other reactive species such as HO₂, which may play an important role in the diamond synthesis. The addition of CO₂ or CO, (having lower critical temperatures and pressures) will likely facilitate retrograde condensation. Furthermore, entrainers such as oxygen can be used to promote oxidation and enhance the formation of CH₃ in solution (which is believed to be the dominant growth precursor in the synthesis of diamond), and therefore enhance the growth rates. Zhao et al.²⁴ have provided the diamond hydrothermal synthesis from the mixture of the glassy carbon, powdered nickel, diamond seeds and water at 800° C and 1.4 kbar. Nakano et al. (ref.6) synthesised the nanodiamonds from the mixture of the interstellar organics with water at 200-400° C. Simakov et al.²⁵ have provided the nanodiamond hydrothermal synthesis from the water-alcohol solutions at 500° C and pressure lower than 1000 bar.

On the other hand, water is known to be an effective solvent for large hydrocarbons and alcohols at relatively low temperatures²⁶. Such an environment is also known to be a suitable reactive environment for the oxidation of organics^{27,28}. It is known that the water-oil solutions are possible in the range of 300-400° C at a pressure of nearly 220 bar^{29,30}. The oil dissolution in water is also increased with the CO₂ and alcohol addition (ref. 29),³¹.

From the above data it's possible to conclude that we could provide the hydrothermal syntheses of nanodiamonds from the water-oil or water-alcohol-oil solutions, based on the known method of nanodiamond syntheses from water-alcohol solutions at P-T parameters corresponding to supercritical water conditions and to the region of oil dissolution in water (ref. 25). As a result, we could come to the creation of low energetically and ecologically industrial method of nanodiamond formation at the utilization of the oil rests at P-T parameters corresponding to the processes of oil and oil rests refine.

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